Synthetic Organic Chemicals

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Natural Gas and Its Uses

THE natural gas industry has lately received much attention in newspapers and magazines. Pipe lines are being extended for long distances from natural gas areas to regions which are accustomed to manufactured gas. The State of California recently passed laws requiring petroleum producing companies to conserve as much as possible of the natural gas output from their oil wells. Bankers and public utility officials have been busy consulting geologists as to the probable life of this valuable natural resource. It is therefore interesting to look into the origin and composition of natural gas and to consider its uses.

The origin of natural gas is probably in the slow decomposition of vegetable matter at low temperatures; a process that has been going on for centuries. It is found only in sedimentary rocks where the porous nature of the limestone and sandstone permits its storage under pressure. It accumulates in large quantities only when there is an impermeable layer of shale or similar material above the porous strata to act as an effective seal. Consequently, natural gas reservoirs may extend over wide areas, although the most effective locations for the outlets are usually at the upper end of an anticlinal or rock wave where the gas collects in pockets. The pressure of the gas depends in a large measure on the depth of the reservoir and is roughly equivalent to the hydrostatic pressure of a column of water of the same depth.

Practically ninety-eight per cent of the world's commercial production of natural gas is accounted for by the United States. Although over half of the states produce some natural gas, the principal fields are located in six states; Oklahoma, Texas, California, Louisiana, West Virginia, and Pennsylvania. Many of these fields supply gas to neighboring states through pipe lines hundreds of miles in length.

Gas wells are drilled in much the same manner as oil wells. The larger ones are tubed and also equipped with gate valves so that the gas can be kept back when not needed in the mains. Several thousand new wells are drilled each year to replace those which have been abandoned, and to take care of the increasing consumption for industrial uses. Powerful compressors are often located at the wells so that larger quantities of gas can be delivered at higher pressures, without increasing the size of the mains.

The principal constituent of natural gas is methane, or marsh gas, CH_4, which most of us remember as the first organic preparation in high school laboratory manuals. Many of the wells average as high as 98% of this elementary hydrocarbon. Some natural gas contains small amounts of ethane, propane, and even higher homologues; West Virginia gas being nearly 14% ethane. "Wet gas" contains pentane, hexane, and heptane, and forms the basis of natural gasolines.

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THE FIRST A.C.S. ORGANIC SYMPOSIUM, Rochester, N. Y., December 29-31, 1925

The THIRD *national symposium on organic chemistry under the auspices of the Organic Division of the American Chemical Society will be held at Princeton, N. J., beginning December 30, 1929*

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These highly volatile substances can be recovered either by slight cooling and compressing, by absorbing in oil and redistilling, or by absorbing on charcoal or other porous material. The product, which is often called casing-head gasoline, owing to its similarity to the gases collecting around the casing heads of oil wells, is used to enrich the gasoline obtained from petroleum refining. Practically all of the natural gas produced today is treated to recover this product, and casing-head gasoline accounts for over ten per cent of gasoline production of this country.

Since it contains only a few per cent of inert components, natural gas has a high fuel value, ranging for different localities from 750 to 1,400 B. T. O. per cubic foot. With plenty of air it burns completely, leaving no liquid or solid residue, therefore its cleanliness is highly valued. For this reason it is used in the manufacture of glass, for heating china kilns and other refractories, for baking enamels, case hardening, and so forth. It has advantages over solid fuel in the lower labor cost and easy temperature control. Since it has no toxic properties, it makes an ideal household fuel. It does, however, form explosive mixtures with air in as small amounts as 20:1 air-gas ratio.

The illuminating properties of the gas depend largely on the ethane content, therefore, natural gas from petroleum fields is more luminous than that occurring in other regions. With the Welsbach type of burner, this property is not so important as in the early days. It is interesting to note in this connection that the first economic development of natural gas in this country was in 1821 when the town of Fredonia, N. Y., installed street lamps supplied from a nearby gas well.

Approximately one tenth of the total production of natural gas is used in the carbon black industry. This commercial pigment used so extensively in printing inks, rubber compounding, and so forth, is made from the incomplete combustion of natural gas. The carbon from the flame is deposited on a slowly rotating metal plate and is scraped off automatically so that little labor is involved. The process does not use the full calorific value of the gas and in many places the manufacture of carbon black is carefully regulated by law.

The synthesis of aliphatic compounds from natural gas has made rapid strides in recent years. Some of these are made by first cracking the hydrocarbons to unsaturated compounds such as ethylene and propylene which are more reactive chemically. Direct chlorination of the former gives ethylene dichloride, while treatment with hypochlorous acid yields ethylene chlorohydrin which on hydrolysis produces ethylene glycol. When absorbed in sulfuric acid, the unsaturated hydrocarbons form the corresponding sulfates which can either be isolated or converted into alcohols. Large quantities of isopropyl alcohol are now made from propylene.

In other synthetic processes, the saturated hydrocarbons are treated directly with chlorine, without any previous cracking. If pentane is vaporized and treated with gaseous chlorine, under pressure, at slightly elevated temperatures, amyl chloride is formed. When hydrolyzed with sodium hydroxide the chloride gives an exceptionally pure grade of amyl alcohol.

The subject of natural gas cannot be left without mentioning the production of helium which forms one to two per cent of the natural gas in some fields. A large government plant is located near Fort Worth, Texas, where the helium is separated by liquefying the other gases present. The production of helium is under government control and large amounts of this non-inflammable gas are being accumulated for future use in dirigibles.

Organic Chemicals as Analytical Reagents

ALIZARIN

Laidlaw and Payne, Biochem. J. *16*, 494 (1922)

The calcium is first separated as the oxalate which after acidifying is treated with a 0.1% solution of alizarin in alcohol. The purple solution on standing for a day precipitates blue-black needles of calcium alizarinate. The alizarin is liberated from this compound by means of oxalic acid. The orange color is then compared with known standards. One-tenth milligram of calcium can be estimated with an accuracy of 0.005 mg.

AMINONAPHTHOL SULFONIC ACID

Roe and Kahn, J. Biol. Chem. Jan., 1929.

Calcium in blood serum is determined indirectly by first precipitating as calcium phosphate, then estimating the phosphorus with acid ammonium molybdate and 1-amino-2-naphthol-4-sulfonic acid. The same reagent can also be used for the direct colorimetric estimation of phosphates in blood and urine.

MALONIC ACID

POTASSIUM CYANATE

Macchia, Chem. Zeit *52*, 281 (1928)

Calcium, strontium, and barium can be detected by the behavior of their malonic salts. The carbonates are dissolved in dilute hydrochloric acid, concentrated to a few cc., then shaken with 0.5 gm. of malonic acid until it is entirely dissolved. After shaking with a slight excess of ammonia, white barium malonate precipitates and is filtered off. The filtrate is diluted to 5 times its volume with methyl alcohol, warmed and allowed to cool, at which time strontium malonate precipitates out and is filtered. The formation of white, flocculent calcium cyanate which redissolves can be observed when the second filtrate is warmed with 20% potassium cyanate.

OLEIC ACID

Gregoire et al. J. S. C. I. *42*, 427A (1923)

In the absence of magnesium, calcium can be determined by the formation of pale yellow colloidal calcium oleate. The reagent consists of 2 gm. of oleic acid and 0.5 gm. of KOH in 600 cc. of alcohol which is later diluted with water to one liter. The sample containing 0.006-0.09 mg. of calcium is placed in a 50 cc. measuring flask and diluted to 45 cc. To this is added 1 cc. of a solution containing 20 gm. of Rochelle salt, and 7.5 gm. of KOH per 100 cc. One cc. of the potassium oleate reagent is added, the mixture shaken, diluted to 50 cc., and compared with a standard after one hour.

THYMOLPHTHALEIN

Schock, Ind. and Eng. Chem. *19*, 112 (1927)

Using thymolphthalein as an indicator it is possible to determine calcium ion by direct titration with standard sodium carbonate solution at temperatures between 90-100° C. A method is described for determining calcium, magnesium, and sulfates, in the same solution, with different reagents, using thymolphthalein as an indicator.

New Chemicals

The following chemicals have been added to our list since the last issue of this bulletin was published:

*Cholesterol Dibromide
*Cyclohexyloxalate
*Cyclohexylphthalate
*Dodecane
Methylethyl-phenylethyl Malonate
*p-Nitrodiphenyl
*Phenylethyl Chloride
Sodium Azide
*Trilaurin
*Zinc Ammonium d-Lactate
*Zinc d-Lactate

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